

Degradation studies of ciprofloxacin on a pillared iron catalyst

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Abstract

Photo-assisted Fenton mineralization of ciprofloxacin (CFX), a broad-spectrum antibiotic used in human and veterinary medicine was studied using a modified laponite clay-based Fe nanocomposite (Fe-Lap-RD) as a heterogeneous catalyst in the presence of hydrogen peroxide and UV light. The catalytic performance has been monitored in terms of CFX (0.15 mM) and total organic carbon (TOC) conversions, whereas the catalyst stability was evaluated according to the metal leached from the solid structure into the aqueous solution. The Fe-Lap-RD was characterized by X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma-atomic emission spectrometry (ICP-AES) techniques. Further, the effects of reaction parameters such as H₂O₂ concentration, Fe-Lap-RD catalyst loading and initial solution pH on the mineralization of CFX were investigated. It was found that at the optimal reaction conditions (60 mM H₂O₂, 1.0 g L⁻¹ Fe-Lap-RD, initial solution pH 3.0), complete CFX degradation and over 57% total organic carbon (TOC) removal of CFX can be achieved after 30 min reaction. In addition degradation and mineralization kinetics of CFX was also studied to obtain apparent reaction rate constants. The photo-Fenton degradation of CFX follows the pseudo-first-order kinetics. Fe-Lap-RD exhibits good catalytic activity in the photodegradation and mineralization of CFX, with negligible leaching of Fe ions from the catalyst structure.

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1. Introduction

Fluoroquinolones (FQs) currently represent one of the most important classes of antibiotics, on the basis of annual global sales and therapeutic versatility [1,2]. FQs are a class of synthetically produced antibiotics, active against a broad spectrum of pathogenic gram-negative and gram-positive bacteria. Consequently, they are used as the antibiotics of first choice for general bacterial infectious diseases, and its efficacies are highly appreciated. Ciprofloxacin, a common FQ, is a primary degradation product of enrofloxacin, which is used worldwide in aquaculture and agricultural applications [1,3]. Because of their continued use in both human and veterinary medicine, the environmental impact of such antibacterial agents represents a serious concern for the public

health due to their potential for migration into the environment and the possible development of resistance in pathogens [4–6].

Ciprofloxacin is readily transported into the environment via discharges of wastewater and direct runoff. It has been repeatedly detected at concentrations ranging from $\mu\text{g L}^{-1}$ in untreated hospital sewage [7–9], to ng L^{-1} levels in secondary wastewater effluents [10–17], and surface waters [9].

At present, most of the wastewater treatment plants are not designed to completely remove most pharmaceuticals, and consequently these compounds are released into receiving water bodies. Advanced oxidation processes (AOPs) are known as an effective method to remove non-biodegradable organic pollutants from ground-, surface- and wastewater [17,18]. Their effectiveness results from the fact that the in situ generated hydroxyl radicals are highly reactive species, able to oxidize organic molecules. The radicals are produced by combinations of ozone, hydrogen peroxide, UV radiation, ferrous ions and titanium dioxide. Numerous authors investigated the degradation of organic pollutants such as pesticides, dyes, pharmaceuticals, aromatic compounds, nitrophenols or surfactants by

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photo-Fenton oxidation [18–23]. Traditionally, the photo-assisted Fenton reaction is conducted homogeneously by irradiating a solution containing Fe^{3+} or Fe^{2+} ions and H_2O_2 . The decomposition of H_2O_2 in an acidic media is catalyzed by the oxidation of Fe^{2+} to Fe^{3+} , which is subsequently photo-reduced back to Fe^{2+} . The hydroxyl radicals formed are responsible for effecting the degradation of organic compounds in the wastewater.

The major disadvantage of such a system is, reactions are to be studied at acidic $\text{pH} < 3$ and it is difficult to remove the sludge containing Fe ions after the treatment. The latter step is expensive and not economical. Extensive information exists on the attempts to find a solid support for the iron ions to eliminate its major disadvantage of homogeneous photo-Fenton process. In a number of studies the development of the heterogeneous photo-assisted Fenton catalyst such as Nafion-based catalysts [24–26] have been reported, but these materials proved to have a low catalytic activity and to be too expensive for an industrial application.

Pillared clays constitute one of the most widely studied materials among the new groups of microporous materials developed by molecular engineering. These solids, also known as cross-linked clays or pillared interlayered clays (PILCs), are obtained by exchanging the interlayer cations of layered clays with bulky inorganic polyoxocations, followed by calcinations. The intercalated polycations increase the basal spacing of the clays and, upon heating, they are converted to metal oxides clusters by dehydration and dehydroxylation. These metal oxide clusters (named pillars), are inserted between the clay layers, yielding temperature-stable oxide pillars that permanently keep the layers apart, preventing its collapse. As a result, an interlayer space of molecular dimensions, a two-dimensional porous network, is generated [27,28]. The final pillared interlayered clays present a permanent porous network, showing a dramatic improvement in catalytic and adsorption applications [29–32].

Recently, numerous studies reported the synthesis of different smectite clay based Fe nanocomposites by pillaring methods and used them as hetero-catalysts for the photo-Fenton decoloration and mineralization of some azo-dyes pigments [29–31,33] and phenyl-urea herbicides [28,34]. In a diluted aqueous dispersion, laponite RD, model synthetic hectorite-type smectite clay, exists as discrete plates of diameter 20–30 nm. Therefore, this clay is an ideal inorganic medium to form nanometer-scale composite structures with iron oxide particulates [30], named Fe-Lap-RD. The X-ray diffraction (XRD) results revealed that the Fe-Lap-RD mainly consists of Fe_2O_3 (maghemite) crystallites and $\text{Fe}_2\text{SiO}_5(\text{OH})_2$ (iron silicate hydroxide) crystallites [33].

A heterogeneous catalyst for photo-Fenton reaction with a high efficiency as well as an acceptable cost has not been fully established. Hence, there is no doubt that developing such a catalyst has not only academic significance but also industrial applications. This type of catalyst displays a reasonable good photo-catalytic activity and negligible Fe leaching at an initial solution pH of 6.6, which is very close to neutral pH [35]. These findings enhance the feasibility of the photo-Fenton process for

the treatment of wastewater, without the need to pre-adjust the solution's pH or to neutralize it at the end.

The objectives of this study are (i) to prepare laponite clay based Fe-nanocomposites by pillaring technique; (ii) to test the catalytic activity of new material as heterogeneous catalysts for the photo-Fenton degradation and mineralization of ciprofloxacin in aqueous solutions; (iii) to describe the effect of the initial pH, hydrogen peroxide concentration and Fe-Lap-RD catalyst loading on the mineralization of ciprofloxacin.

2. Materials and methods

2.1. Materials

Ciprofloxacin (Fig. 1) was supplied by BioChemika, Fluka (Steinheim, Germany). *Ortho*-phosphoric acid (98%), hydrogen peroxide (30%), iron sulphate heptahydrate, sodium hydroxide, hydrochloric acid, manganese dioxide were provided by Merck (Darmstadt, Germany). All other chemicals and solvents were of the highest grade commercially available and were used as obtained. All aqueous solutions were prepared with ultrapure water from a Millipore Waters Milli-Q purification water unit (Millipore, Watford, UK).

The synthetic layered clay laponite (laponite RD) was supplied by Kremer Pigments, Germany and it was used as the starting clay material to prepare the Fe-Lap-RD nanocatalyst. Table 1 presents the chemical composition of the commercial clay supplied by the company as described above. Iron(III) nitrate nano-hydrate, received from Aldrich, was used as iron source. Sodium carbonate deca-hydrate was obtained from Fluka.

2.2. Preparation of Fe-Lap-RD nanocomposite

The Fe-Lap-RD nanocatalyst was synthesized through a reaction between a solution of iron salt and a dispersion of laponite RD clay [28,34]. For that purpose an aqueous dispersion of laponite RD was prepared by adding 2 g of clay to 100 mL water under vigorous stirring condition. Secondly, sodium carbonate was added slowly as powder into a vigorously stirred 0.2 M solution of iron nitrate such that a molar ratio of 1:1 for $\text{Na}^+/\text{Fe}^{3+}$ was established. Subsequently, the obtained solution was added into the dispersion of laponite

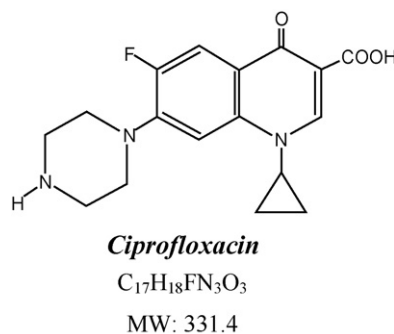


Fig. 1. The structure of ciprofloxacin [1-cyclopropyl-6-fluoro-4-oxo-7-piperazin-1-yl-quinoline-3-carboxylic acid].

Table 1
Composition of commercial laponite clay

Component	Amount (%)
SiO ₂	59.5
MgO	27.5
Li ₂ O	0.8
Na ₂ O	2.8
Loss on ignition	8.2

clay prepared in the first step. The ratio of iron cations to clay was 11 mmol Fe³⁺ per gram clay. In a dilute aqueous dispersion, the clay exists as discrete plates of diameter 20–30 nm. Fe₂O₃ can be readily intercalated as pillars. Hence, it is possible to prepare a clay-based composite containing nano-sized Fe₂O₃.

The suspension was stirred for 2 h followed by thermal aging and placed in an oven at 100 °C for 2 days. The precipitate was collected and washed with deionized water several times to ensure all Na ions were removed. The recovered material was dried under the fume board at room temperature in air and after calcination at 350 °C for 20 h the nanocomposite was obtained and named as Fe-Lap-RD.

2.3. Analytical instruments

HPLC analyses were carried out on an Agilent 1100 series LC chromatograph system (Agilent Technologies, Germany) equipped with a binary pump, a degasser, an auto-sampler, a ALS column thermostat, a UV–vis diode array detector and a FLD detector. Chromatographic separation was performed on reversed phase column (RP Luna C18(2) Phenomenex, 5 µm, 150 mm × 4 mm i.d.) equipped with an ODS, Octadecyl guard column (Phenomenex). Isocratic elution was performed at 30 °C, for a flow rate of 0.8 mL min^{−1}, using solvents A (0.02 M *o*-H₃PO₄) and B (acetonitrile) in a proportion of 85% A and 15% B. The injection volume was 25 µL and the DAD detection wavelength was set at 280 nm. For the measurement of lower concentration the fluorescence detection ($\lambda_{\text{ex}} = 278$ nm and $\lambda_{\text{em}} = 455$ nm) was used.

The total organic carbon (TOC) value of the reaction solution was monitored with a Shimadzu model 5050 TOC analyzer equipped with an auto-sampler. Chemical oxygen demand (COD) determination was conducted with commercially available test kits of the company Machery and Nagel, Düren, Germany. The consumption of H₂O₂ during the reaction was followed by Quantofix Peroxide 25 sticks (Machery and Nagel, Düren, Germany). The pH and conductivity values were measured by means of a WTW pH-Meter Multiline P4.

The chemical composition of Fe-Lap-RD was determined through the X-ray photoelectron spectroscopy (XPS), using a VG Scientific Microlab Mk III with a monochromatic Al K α source ($h\nu = 1486.6$ eV) [36].

An ICP-AES “JY 70 plus” system (Jobin Yvon, Long-Jumeau, France) was used for Mg and Fe determinations in order to characterize the new catalyst. Sample introduction was performed by a peristaltic pump (1.5 mL min^{−1}, Abimed, Langenhagen, Germany), connected to a Meinhard nebulizer

which fitted into a cyclone spray chamber. The measured spectral element lines were: Mg, 279.079 nm and Fe, 259.941 nm. The RF power was set to 1000 W, the plasma gas was 15 L Ar min^{−1}, whereas the nebulizer gas was 600 mL Ar min^{−1}. These parameters were the optimal conditions for this instrument. The amount of Fe leaching from the Fe-Lap-RD in reaction solution versus time was measured by Nanocolor commercially available kits (Machery and Nagel, Düren, Germany).

2.4. Evaluation of the photo-catalytic activity

The photo-catalytic activity of Fe-Lap-RD nanocatalyst was tested in the degradation and mineralization of 0.15 mM ciprofloxacin solution at a constant temperature of 298 K, in a cylindrical batch photo-reactor. A mercury high-pressure lamp (HPK 125 W Philips) with a water-cooled filter served as a light source. The total reaction volume was 0.15 L. The intensity of photonic flux (9×10^4 µEs m^{−2} s^{−1}) was measured with a Li-COR model 185 A radiometer/quantum/photometer. In order to establish a good dispersion of the Fe-Lap-RD catalyst in the antibiotic solution, air was bubbled from the bottom to the top.

The starting point of the reaction is defined as the time when the UVC light was turned on and a certain amount of H₂O₂ was added to the ciprofloxacin solution. To assess the ciprofloxacin (CFX) conversion, TOC removal and the leachate of Fe ion from the Fe-Lap-RD nanocatalyst, a known volume of sample solution was withdrawn from the photo-reactor at regular time interval. The Fe-Lap-RD nanocatalyst was separated from the sample solution by filtration with Sartorius cellulose nitrate filter (pore diameter 0.1 µm).

3. Results and discussion

3.1. Characterization results of Fe-Lap-RD

The synthesized Fe-Lap-RD was characterized by inductively coupled plasma-atomic emission spectrometry (ICP-AES) and XPS techniques.

The element concentrations detected by ICP are presented in Table 2. The iron mass concentration with respect to the total mass of Fe-Lap-RD was determined to be 30% (wt.%).

The quantitative surface chemical composition of the Fe-Lap-RD nanocomposite was evaluated by XPS technique [34]. The binding energy of the identification peaks and the surface atomic concentrations of main elements, Fe, Mg, O, Si and C, are listed in Table 3. The active site could be Fe containing points that can accelerate the decomposition of H₂O₂ in the presence of UV light [30]. The Fe surface atomic concentration

Table 2
Element concentrations (%) before and after irradiation using a mercury high-pressure lamp (4 × 0.5 h)

Element	λ (nm)	Before reaction	After reaction
Fe	259.941	30.90	30.10
Mg	279.079	4.82	3.32

Table 3

The binding energy (eV) and the atomic concentrations (at.%) for Fe-Lap-RD before and after irradiation using a mercury high-pressure lamp (4×0.5 h)

Element	Binding energy (eV)		at.%	
	Before reaction	After reaction	Before reaction	After reaction
Mg(1s)	1306.65	1303.65	9.78	9.75
Fe(2p _{3/2})	713.85	711.30	6.11	6.09
O(1s)	534.50	531.60	59.04	59.06
C(1s)	287.40	284.80	5.27	5.31
Si(2p)	105.15	102.35	18.08	18.08

of Fe-Lap-RD determined by XPS was 6.11%. The binding energy of the Fe in the catalyst before reaction was determined to be 713.85 eV (Table 3). It is assumed that the detected Fe is caused mainly by Fe^{3+} ions and not by the Fe in zero oxidation state [30,37]. The detailed XPS spectra of the catalyst is shown in Fig. 2 (curve A).

The value for the Fe concentration with respect to the total weight (30.9%), measured by ICP-AES technique is close to the Fe mass concentration determined by X-ray reflective fluorescence (27.3 wt.%) [29]. Iron surface atomic concentration of 6.11% determined by XPS and the values found for the binding energy of the identification peaks are in accordance with the results reported by Feng et al. [29,35]. The authors used the same procedure to prepare Fe-Lap-RD as we did.

3.2. Photo-catalytic activity of Fe-Lap-RD catalyst

The photo-catalytic activity of the Fe-Lap-RD was examined in the photo-assisted degradation of ciprofloxacin in the presence of H_2O_2 and UV light. The efficiency of photo-Fenton reactions depends on parameters like the initial pH value and the concentrations of involved reactive species.

Ciprofloxacin concentration versus irradiation time was determined by HPLC measurements and the conversion of the original substrate, X_{CFX} (%), was used to define the efficiency of the degradation.

$$X_{\text{CFX}} = 100 \left(1 - \frac{C_{\text{CFX}}}{C_{\text{CFX}}^0} \right) \quad (1)$$

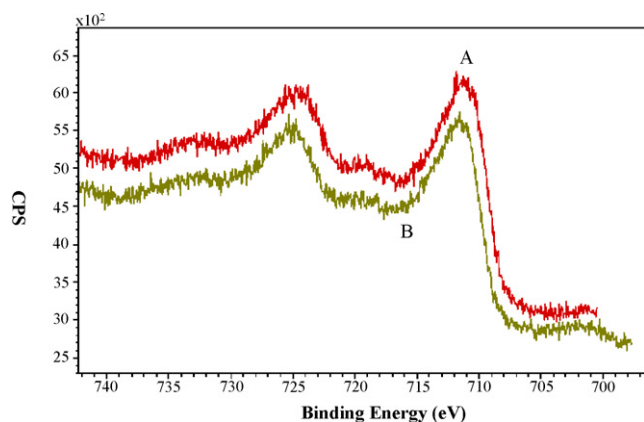


Fig. 2. X-ray photoelectron spectroscopy (XPS) spectra of the Fe(2p_{1/2}) and Fe(2p_{3/2}) regions of Fe-Lap-RD: before (A) and after 4×0.5 h reaction (B).

where C_{CFX} and C_{CFX}^0 refers to the ciprofloxacin molar concentrations values at reaction time τ and 0, respectively.

The complete conversion of ciprofloxacin molecule leads to the reaction intermediates accumulation. Cardoza et al. [38] describe that photo-degradation of ciprofloxacin leads to transformation products resulting from the decomposition of the piperazine ring, additions of hydroxyl radicals to the aromatic ring and functional groups substitutions or loss. Fluoroquinolones' ability to inhibit bacterial DNA replication and repair is believed to be linked to their quinolone moieties, suggesting that piperazine fragmentation may not lead to elimination of antibacterial activity [1]. In order to assess the mineralization degree the total organic carbon values were recorded during the photo-degradation procedures.

The TOC removal ratio of the reaction solution was defined as below:

$$X_{\text{TOC}} = 100 \left(1 - \frac{\text{TOC}}{\text{TOC}_0} \right) \quad (2)$$

where TOC and TOC_0 refer to the TOC values at reaction time τ and 0, respectively.

The kinetics in this study only refers to apparent reaction kinetics considering that several processes can contribute to the overall degradation of CFX: (i) adsorption of CFX on the catalyst, (ii) CFX oxidation by hydroxyl radicals coming from heterogeneous photo-Fenton reaction, or (iii) CFX oxidation by hydroxyl radicals coming from direct photolysis of H_2O_2 .

The apparent degradation kinetics of CFX in aqueous solution is described according the pseudo first-order equation:

$$-\frac{dC_{\text{CFX}}}{d\tau} = k_{\text{ap,c}} C_{\text{CFX}} \quad (3)$$

where C_{CFX} is the CFX's molar concentration in water, τ the reaction time and $k_{\text{ap,c}}$ is the pseudo first-order rate constant. By plotting $-\ln(C/C_0)$ as a function of reaction time τ , through linear regression, the $k_{\text{ap,c}}$ constants could be derived from the slopes of the straight lines, through linear regression, using the experimental data. The TOC removal rate was also expressed by a first-order kinetic equation which became by integration:

$$\ln \frac{\text{TOC}_0}{\text{TOC}} = -\ln(1 - X_{\text{TOC}}) = k_{\text{ap,TOC}} \tau \quad (4)$$

where $k_{\text{ap,TOC}}$ stands for the apparent mineralization rate constant. The $k_{\text{ap,c}}$ and $k_{\text{ap,TOC}}$ values calculated from the experimental data, using the method as given above, are listed in Table 4.

3.2.1. Influence of hydrogen peroxide concentration

In a Fenton based system the H_2O_2 molar concentration is a key factor that can significantly influence the degradation of organic compounds. The hydrogen peroxide concentration is directly related to the number of hydroxyl radicals generated in the photo-Fenton reaction. The optimal value for hydrogen peroxide concentration (60 mM) at pH 3 and at a concentration of 1 g L^{-1} Fe-Lap-RD is given in Table 4. pH 3 was chosen as the initial solution pH since best performance for the photo-Fenton reaction was achieved at pH values between 2.8 and 3.0.

Table 4

Rate constants at different operational parameters (30 min, irradiation 25 °C, $C_{\text{CFX}}^0 = 0.15 \text{ mM}$)

No.	C_{CFX}^0 (mM)	pH	$C_{\text{Fe-Lap-RD}}$ (g L ⁻¹)	$k_{\text{ap,c}} (\times 10^{-3} \text{ s}^{-1})$	$k_{\text{ap,TOC}} (\times 10^{-4} \text{ s}^{-1})$
1	0	3	1.00	$0.972 \pm 7.53\%$	$1.777 \pm 6.12\%$
2	3	3	1.00	$2.166 \pm 3.09\%$	$2.749 \pm 5.94\%$
3	6	3	1.00	$2.333 \pm 3.68\%$	$3.333 \pm 9.84\%$
4	12	3	1.00	$2.722 \pm 6.53\%$	$3.444 \pm 4.10\%$
5	24	3	1.00	$3.333 \pm 7.21\%$	$4.222 \pm 6.86\%$
6	36	3	1.00	$4.416 \pm 6.07\%$	$5.061 \pm 6.81\%$
7	60	3	1.00	$5.555 \pm 10.21\%$	$5.333 \pm 8.51\%$
8	60	4	1.00	$3.166 \pm 9.03\%$	$4.140 \pm 7.90\%$
9	60	5	1.00	$1.444 \pm 8.41\%$	$3.555 \pm 8.88\%$
10	60	6	1.00	$1.222 \pm 1.97\%$	$3.122 \pm 5.35\%$
11	60	7	1.00	$8.888 \pm 2.83\%$	$2.833 \pm 2.55\%$
12	60	10	1.00	$6.666 \pm 4.59\%$	$1.555 \pm 9.80\%$
13	24	3	0.00	$1.338 \pm 7.72\%$	$0.830 \pm 8.48\%$
14	24	3	0.25	$2.108 \pm 6.83\%$	$1.444 \pm 6.86\%$
15	24	3	0.50	$2.806 \pm 4.57\%$	$1.889 \pm 10.02\%$
16	24	3	1.50	$3.329 \pm 2.18\%$	$2.944 \pm 3.53\%$

Fig. 3A presents the CFX degradation as a function of the reaction time at different H_2O_2 concentrations. When the experiment is conducted with 1.0 g L^{-1} Fe-Lap-RD and UV light without H_2O_2 , the CFX concentration decreases from

0.15 mM to 0.03 mM during the first 25 min ($X_{\text{CFX}} = 80\%$). No further acceleration of the conversion is observed till the end of the treatment. This fast but limited decrease of CFX concentration during the first 25 min is most probably caused by the adsorption of CFX on the Fe-Lap-RD surface [30].

The CFX concentration decreases much faster in the presence of hydrogen peroxide, 1.0 g L^{-1} Fe-Lap-RD and UV irradiation. The increase of H_2O_2 concentration has a beneficial effect on the mineralization of ciprofloxacin until a critical H_2O_2 concentration is achieved (Fig. 3B). As H_2O_2 increases, the conversion and mineralization accelerates up to 60 mM H_2O_2 . The mineralization of CFX is greatly enhanced most likely due to the formation of more $\cdot\text{OH}$ radicals at higher H_2O_2 concentrations of the test solution.

However, when the concentration of H_2O_2 is higher than its critical concentration, no further acceleration in the mineralization degree occurs. This phenomenon could be explained by the scavenging effect of excess H_2O_2 , which will decrease the number of $\cdot\text{OH}$ radicals in the solution. As shown in Fig. 4, the optimal concentration of hydrogen peroxide for the studied system seems to be achieved by a concentration of 60 mM H_2O_2 already after 30 min of irradiation indicating the decomposition degree (COD) of ciprofloxacin is total.

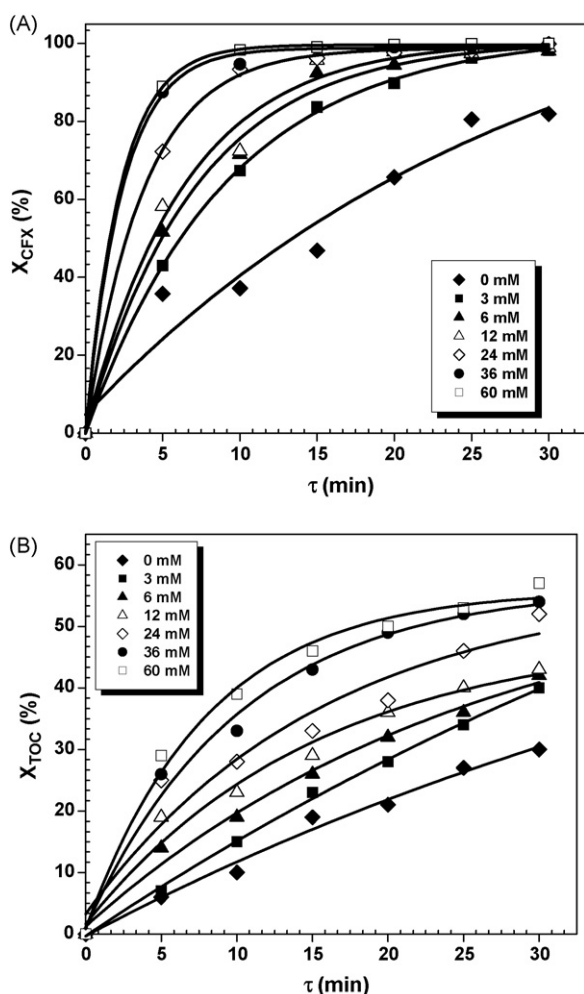


Fig. 3. Influence of hydrogen peroxide concentration on ciprofloxacin (0.15 mM) conversion (A) and on the mineralization degree (B) (25 °C, pH 3, 1 g L^{-1} Fe-Lap-RD).

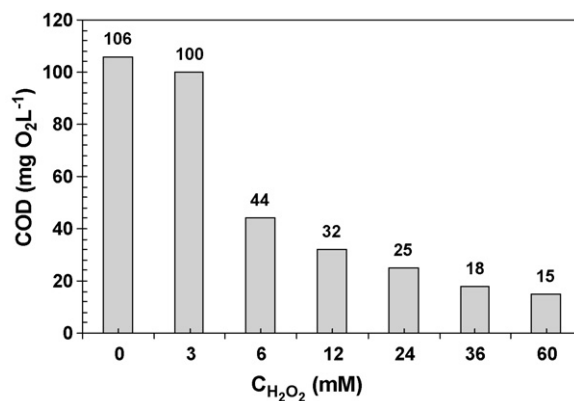
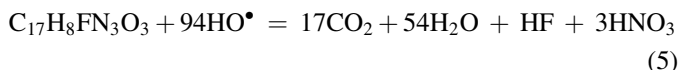


Fig. 4. The influence of hydrogen peroxide concentration on COD uptake after 30 min irradiation (25 °C, pH 3, 1 g L^{-1} Fe-Lap-RD, $\text{COD}_0 = 124 \text{ mg O}_2 \text{ L}^{-1}$).

The optimal hydrogen peroxide concentration was found to be 60 mM H_2O_2 , for 0.15 mM ciprofloxacin solution, at pH 3 and 1 g L^{-1} Fe-Lap-RD. The overall stoichiometry for the mineralization of CFX by $\bullet\text{OH}$ radicals can be written as:



On the basis of this equation, 47 mol of H_2O_2 are theoretically needed to completely degrade 1 mol of ciprofloxacin. In the present study, the optimal $[\text{H}_2\text{O}_2]/[\text{CFX}]$ molar ratio equals 400. This value is eight times larger than the theoretical value. These results are in accordance with the previous findings of [30] obtained by the mineralization of an azo dye, Orange II, using Fe-Lap-RD. It can be concluded that an excess amount of H_2O_2 is required to reach the maximum degradation of ciprofloxacin. The importance of the optimal dose of H_2O_2 has been proved during the Fe-Lap-RD/UV/ H_2O_2 degradation of pollutants such as phenyl-urea pesticides [34] and azo-dyes pigments [31,32].

3.2.2. Effect of the Fe-Lap-RD catalyst loading

Catalyst loading is an important factor significantly influencing the heterogeneous photo-Fenton reaction. Obtained results indicate that higher catalyst loading leads to a faster degradation of the organic compounds until the saturation is achieved. Fig. 5A illustrates the effect of Fe-Lap-RD catalyst loading on the conversion of ciprofloxacin in the presence of 24 mM hydrogen peroxide. The increase of solution catalyst's loading from 0 to $1 \text{ g Fe-Lap-RD L}^{-1}$ leads to an enhancement of the CFX conversion (Fig. 5A) and of TOC removal ratio of the 0.15 mM ciprofloxacin solution (Fig. 5B).

However, it should be pointed out that when the catalyst concentration is higher than 1.0 g L^{-1} , the efficiency does not increase significantly. Therefore, the optimal Fe-Lap-RD loading for 0.05 mg L^{-1} ciprofloxacin in the presence of 24 mM H_2O_2 and UV light can be considered as 1.0 g L^{-1} Fe-Lap-RD.

In the absence of Fe-Lap-RD, the CFX conversion after 30 min is almost complete (81%) but the TOC removal is very low (13%). Organic substrate oxidation is attributed to $\bullet\text{OH}$ radicals, caused by the direct photolysis of H_2O_2 in the presence of UV irradiation. Lower TOC removal demonstrates that the hydroxyl radicals generated from the direct UV-C photolysis of H_2O_2 is not sufficient for a complete oxidization of CFX and its intermediates. It can be assumed that numerous $\bullet\text{OH}$ radicals decay before they meet the organic molecules. UV-C/ H_2O_2 processes seem to oxidize CFX into some longer-lived reaction intermediates and cannot achieve mineralization [24].

The pseudo-first order rate constants for ciprofloxacin mineralization for different catalyst concentrations are given in Table 4. As shown, mineralization rate constants increase from $0.83 \times 10^{-4} \text{ s}^{-1}$ in the absence of catalyst to $4.22 \times 10^{-4} \text{ s}^{-1}$ when 1 g L^{-1} Fe-Lap-RD is added to the irradiated reaction solution.

As can be seen in Table 4, an addition of Fe-Lap-RD increases the degradation rate of the antibiotic significantly, most probably due to the following processes: (i) adsorption of CFX on the

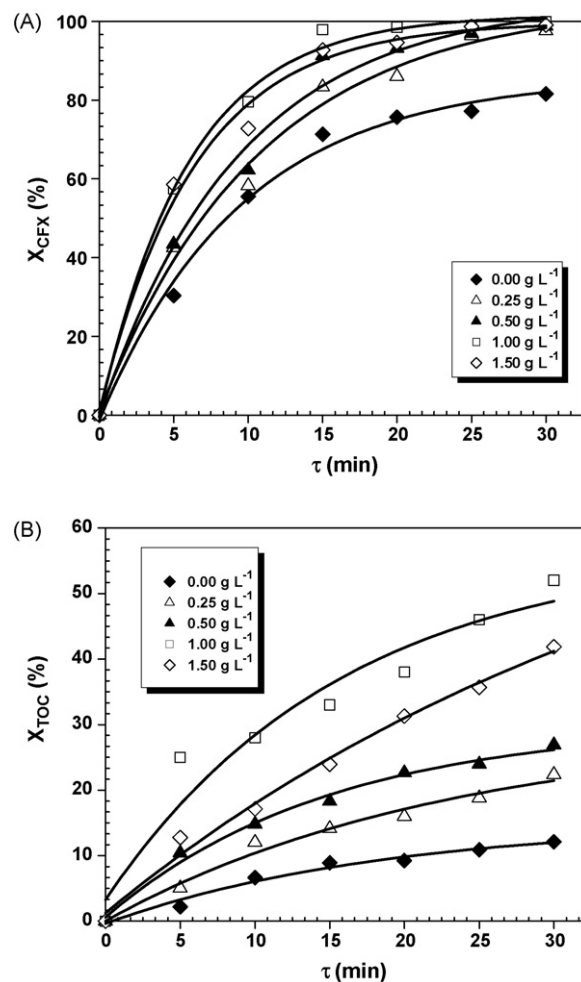


Fig. 5. Effect of the Fe-Lap-RD catalyst loading on ciprofloxacin (0.15 mM) conversion (A) and mineralization degree (B) (24 mM H_2O_2 , 25 °C, pH 3).

surface of the catalyst; (ii) oxidation by $\bullet\text{OH}$ radicals formed by reaction of Fe^{2+} on the surface of Fe-Lap-RD and H_2O_2 ; or (iii) oxidation by homogeneous photo-Fenton reaction due to the Fe ions leached from the catalyst structure in an acidic solution.

Fe-Lap-RD influences the mineralization process in two different ways, namely either as a heterogeneous catalyst that can significantly speed up the decomposition of hydrogen peroxide, producing $\bullet\text{OH}$ radicals. Hence, more catalyst will substantially result in more hydroxyl radicals until a saturated catalyst loading is achieved. Or, due to the small particle size of the catalyst, in this case the solution becomes very turbid particularly when Fe-Lap-RD in solution increases. This might lead to a decreased penetration of UV light, resulting in a decrease of the $\bullet\text{OH}$ radicals formation. It can be concluded that the overall mineralization of ciprofloxacin depends on the combination of described processes and on an optimal Fe-Lap-RD solution loading which leads to a maximum TOC removal.

3.2.3. Influence of pH-value on photo-Fenton degradation

Numerous authors studied the importance of the solution pH by photo-Fenton processes [30,39–41] which influences significantly the photo-Fenton degradation of organic compounds. It has been reported that photo-Fenton process can

remove pollutants under acidic condition and by an optimal solution pH of approximately 3 [42–45]. The results of our previous study [46] also confirm this conclusion. At a pH below 3, the scavenging effect of the hydroxyl radicals by H^+ is severe, while $pH > 3$, the formation of $\cdot OH$ radicals slows down due to the hydrolysis of Fe(III) and the precipitation of FeOOH from the solution [45].

The results on the effect of initial pH solution on the mineralization and degradation of 0.15 mM ciprofloxacin in the presence of 60 mM H_2O_2 , 1.0 g L^{-1} Fe-Lap-RD and UV light are given in Fig. 6. Obviously, the initial pH can significantly influence the degradation kinetics of the test solution. The new Fe-Lap-RD catalyst, exhibited the best catalytic activity at pH 3 while a decreased catalytic activity was observed when the initial solution pH increased from 3 to 10. These results are in agreement with the findings of Pignatello [39] and Feng et al. [30,35]. Even at pH 7, complete degradation of original substrate could still be achieved within 30 min, implying that the Fe-Lap-RD catalyst continue to exhibit a good catalytic activity at higher pH values.

A further aim of this study was to gain information on the mineralization of 0.15 mM ciprofloxacin under the studied conditions (Fig. 6B). Even if the complete degradation can be

achieved within 30 min, some intermediates might still be formed having a higher toxic potential than the parent compound. The environmental risk posed by a contaminant is not necessarily reduced by degradation of the parent compound. Even through the parent compound may not be persistent under the relevant environmental conditions, the transformation products formed may lengthen or even enhanced the harmful effect of a contaminant [38,47].

As can be seen in Table 4, initial solution pH can noticeably influence the mineralization of 0.15 mM ciprofloxacin. At an initial solution pH of 3, the conversion of the substrate is complete and a mineralization degree of 57% is achieved after 30 min reaction, indicating that Fe-Lap-RD nanocomposite exhibited the highest catalytic activity at this pH. As the initial solution pH increases from 3.0 to 10.0, the mineralization kinetics becomes slower, indicating a decrease of photo-catalytic activity. Further it should be noticed that even if the initial solution pH is higher than 3 (4–7), a mineralization degree of 42–47% still can be achieved after 30 min irradiation, indicating Fe-Lap-RD still exhibits reasonable activity even if the initial solution pH is almost neutral. Our results are in agreement with those observed for the photo-assisted Fenton degradation of Orange II [35] and acid black 1 [32]. The authors tested series of pillared laponite clay-based nanocomposites (denoted as Fe-Lap-RD and Fe-B (Fe supported on bentonite clay)) to determine the effect of pH on the discoloration and mineralization of two dyes as mentioned above. They conclude that Fe-Lap-RD nanocomposite is a promising heterogeneous catalyst for the photo-Fenton mineralization of organic compounds.

3.3. Catalyst stability at acidic pH

The complete degradation of ciprofloxacin was achieved in less than 30 min. In order to determine whether the fast degradation of ciprofloxacin results from the presence of Fe-Lap-RD itself or by Fe ions in solution, the iron concentration of the solution was measured as a function of time (Fig. 7). It

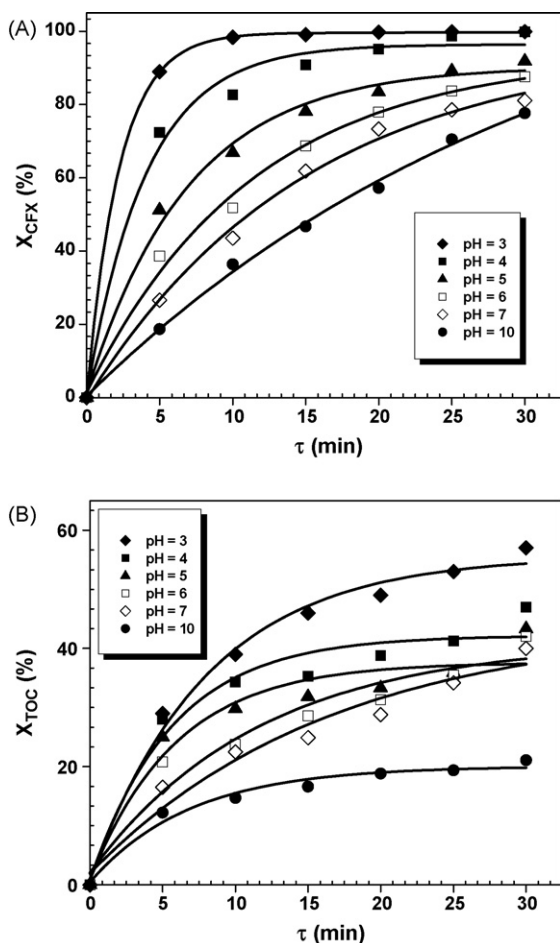


Fig. 6. Effect of initial solution pH on the conversion (A) and mineralization degree (B) of 0.15 mM ciprofloxacin in the presence of 60 mM H_2O_2 , 1.0 g L^{-1} Fe-Lap-RD and 25 °C.

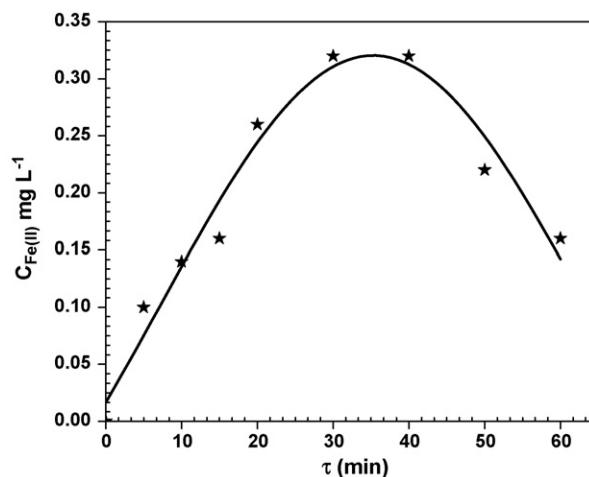


Fig. 7. Fe concentration in solution versus time during 0.15 mM ciprofloxacin degradation in the presence of 60 mM H_2O_2 , 1.0 g L^{-1} Fe-Lap-RD and UV light at 25 °C.

shows that the iron concentration increases approximately to 0.32 mg L^{-1} after 30 min and decreases after 30 min exposure time. The measured Fe ion concentration in solution is less than 1 mg L^{-1} , indicating that the amount of iron ions leaching out from the Fe-Lap-RD is insignificant. Feng et al. [29] observed the same phenomena when they studied the catalytic activity of the Fe-Lap-RD in the photo-assisted degradation of organic azo dye Orange II. The authors further confer that the Fe ion concentration's variation is unclear.

The iron leaching from Fe-Lap-RD is associated with some reaction intermediates such as oxalic acid that can capture Fe ions and form Fe complexes, then going into solution [35]. When the concentration of the intermediates attains maximum, the Fe concentration also exhibits a peak value. While the intermediates are mineralized into CO_2 and H_2O , the Fe ions return to the surface of the catalyst.

3.4. Long-term stability

The long-term stability of a catalyst is a key issue for its industrial application. If the stability is short-dated or deactivation of the catalyst is severe, further investigations or recommendation for an industrial application would not make a sense [30]. To investigate the stability of the Fe-nanocomposite, the catalyst was additionally examined after multiple runs ($4 \times 0.5 \text{ h}$ of reaction) at pH 3 by ICP-AES and XPS, respectively.

The iron and magnesium bulk contents of the catalyst after reaction were determined by ICP-AES and are listed in Table 2 for comparison. As can be seen from the presented results, the difference between the two samples is not significant, indicating that no obvious changes occurred during the catalytic reaction.

In order to demonstrate the structure stability of the Fe-Lap-RD, detailed spectra of the Fe-Lap-RD after $4 \times 0.5 \text{ h}$ of reaction was recorded by XPS. In Table 3 the surface chemical composition of the nanocomposite after $4 \times 0.5 \text{ h}$ reaction time is given. In Fig. 2 (curve B) the oxidation state of Fe in the catalyst determined by XPS and the spectra of Fe(2p_{1/2}) and Fe(2p_{3/2}) regions of the catalyst are shown. No significant changes were observed for all the investigated elements, implying that the obtained catalyst is chemically stable during the photodegradation of ciprofloxacin. Feng et al. [29–31] reported the same phenomena during Orange II and Reactive Red HE-3B mineralization by heterogeneous photo-Fenton reaction.

Considering the results of ICP-AES and XPS measurements, after multiple runs ($4 \times 0.5 \text{ h}$ of reaction) at pH 3, it can be concluded that the catalyst structure does not change during the photo-degradation of CFX, demonstrating good catalytic activity for a long term.

4. Conclusions

The laponite RD clay-based Fe-nanocomposite (Fe-Lap-RD) has been successfully synthesized through a reaction between a solution of iron salt and an aqueous dispersion of laponite RD clay. The catalyst was characterized by ICP-AES

and XPS techniques. The photo-catalytic activity of the Fe-Lap-RD was evaluated in the photo-assisted degradation of a fluoroquinolone antibiotic, ciprofloxacin. The Fe concentration of Fe-Lap-RD with respect to the total weight determined by ICP-AES was 30.9% and the Fe surface atomic concentration determined by XPS was 6.11%.

Both degradation and mineralization of ciprofloxacin by using the laponite clay-based Fe nanocomposite (Fe-Lap-RD) as a heterogeneous catalyst in the presence of hydrogen peroxide and UV light were studied. The initial value of pH, H_2O_2 concentration and catalyst loading are the main factors that can significantly influence the mineralization of CFX. At optimal experimental condition ($60 \text{ mM H}_2\text{O}_2$, 1 g L^{-1} Fe-Lap-RD and pH 3), complete conversion of 0.15 mM ciprofloxacin solution can be achieved within 30 min. Under the same experimental conditions a mineralization degree of 57% was achieved. This difference is due to the complex reaction mechanisms with the formation of intermediates less reactive than CFX.

The nanocomposite exhibited the best photo-activity at an initial solution pH of 3, and the activity decreases as the initial solution pH increases. However, Fe-Lap-RD demonstrates a reasonable good photo-catalytic activity even at an initial solution pH of 7. These characteristics make the catalyst feasible for the photo-Fenton process to treat the original wastewater without the need of pH pre-adjustment of the wastewater effluents or process lines.

As the catalyst loading increases, the degradation of CFX also increases until a saturated catalyst loading is achieved. The saturation catalyst loading is about 1.0 g L^{-1} Fe-Lap-RD. The Fe leaching from the Fe-Lap-RD catalyst is very low and multi-run experiments results revealed that the synthesized material could have a long-term stability for the degradation and mineralization of ciprofloxacin. This study illustrates the possibility of photo-assisted degradation of organic pollutants at neutral pH and without the removal of the iron ions after reaction.

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References

- [1] M.C. Dodd, A.D. Shah, U. von Gunten, U.C.-H. Huang, *Environ. Sci. Technol.* 39 (2005) 7065–7076.
- [2] Y. Pico, A. Vicente, *Anal. Bioanal. Chem.* 387 (2007) 1287–1299.
- [3] L.A. Cardoza, V.K. Almeida, A. Carr, C.K. Larive, D.W. Graham, *Trends Anal. Chem.* 22 (2003) 766–775.

- [4] B. Halling-Sorensen, S.N. Nielsen, P.F. Lanzky, F. Ingerslev, H.C. Luthorft, S.E. Jorgensen, *Chemosphere* 36 (1998) 357–393.
- [5] A. Alonso, P. Sanchez, J.L. Martinez, *Environ. Microbiol.* 3 (2001) 1–9.
- [6] S.B. Levy, B. Marshall, *Nat. Med.* 10 (2004) S122–S129.
- [7] A. Hartmann, E.M. Golet, S. Gartiser, A.C. Alder, T. Koller, R. Widmer, *Arch. Environ. Contam. Toxicol.* 36 (1999) 115–119.
- [8] R. Hirsch, T.A. Ternes, A. Mehling, F. Ballwanz, K.-L. Kratz, K. Haberer, *J. Chromatogr. A* 815 (1998) 213–223.
- [9] E.M. Golet, I. Xifra, H. Siegrist, A.C. Alder, W. Giger, *Environ. Sci. Technol.* 37 (2003) 3243–3249.
- [10] E.M. Golet, A.C. Alder, W. Giger, *Environ. Sci. Technol.* 36 (2000) 3645–3651.
- [11] X.-S. Miao, F. Bishay, M. Chen, C.D. Metcalfe, *Environ. Sci. Technol.* 38 (2004) 3533–3541.
- [12] S. Castiglioni, R. Bagnati, D. Calamari, R. Fanelli, E. Zuccato, *J. Chromatogr. A* 1092 (2005) 206–215.
- [13] K. Mitani, H. Kataoka, *Anal. Chim. Acta* 562 (2006) 16–22.
- [14] K.D. Brown, J. Kulis, B. Thomson, T.H. Chapman, D.B. Mawhinney, *Sci. Total Environ.* 366 (2006) 772–783.
- [15] K.G. Karthikeyan, M.T. Meyer, *Sci. Total Environ.* 361 (2006) 196–207.
- [16] L.A. Batt, B.I. Bruce, S.D. Aga, *Environ. Pollut.* 142 (2006) 295–302.
- [17] S. Parsons, *Advanced Oxidation Processes for Water and Wastewater Treatment*, IWA Publishing, London, UK, 2004.
- [18] K. Ikehata, N.J. Naghashkar, M. Gamal El-Din, *Ozone Sci. Eng.* 28 (2006) 353–414.
- [19] Y. Sun, J.J. Pignatello, *Environ. Sci. Technol.* 27 (1993) 304–310.
- [20] B. Ruppert, R. Bauer, G. Heisler, S. Novalic, *Chemosphere* 3 (1993) 347–399.
- [21] M. Ravina, L. Campanella, J. Kiwi, *Water Res.* 36 (2002) 3553–3560.
- [22] M. Neamtu, A. Yediler, I. Siminiceanu, A. Kettrup, *J. Photochem. Photobiol. A* 161 (2003) 87–93.
- [23] M. Bobu, S. Wilson, T. Greibrokk, E. Lundanes, I. Siminiceanu, *Chemosphere* 63 (2006) 1718–1727.
- [24] J. Fernandez, J. Bandara, A. Lopez, P. Albers, J. Kiwi, *Chem. Commun.* 14 (1998) 1493–1494.
- [25] G. Li Puma, P.L. Yue, in: *Proceedings at the Sixth International Conference on Advanced Oxidation Technologies for Water and Air Remediation*, London, Ontario, Canada, June 26–30, (2000), p. 105.
- [26] S.H. Bossmann, E. Oliveros, S. Gob, M. Kantor, L. Lei, P.L. Yue, A.M. Braun, *Water Sci. Technol.* 44 (2001) 257–262.
- [27] A. Gil, L.M. Gandia, M.A. Vicente, *Catal. Rev.-Sci. Eng.* 42 (2000) 145–212.
- [28] M. Bobu, I. Siminiceanu, *NANOMAT 2005 National Workshop on Nanostructured Materials*, Iasi, Romania, March 24–25, (2005), p. 13.
- [29] J. Feng, X. Hu, P.L. Yue, H.Y. Zhu, G.Q. Lu, *Chem. Eng. Sci.* 58 (2003) 679–685.
- [30] J. Feng, X. Hu, P.L. Yue, H.Y. Zhu, G.Q. Lu, *Ind. Eng. Chem. Res.* 42 (2003) 2058–2060.
- [31] J. Feng, X. Hu, P.L. Yue, H.Y. Zhu, G.Q. Lu, *Water Res.* 37 (2003) 3776–3784.
- [32] O. Sum, J. Feng, X. Hu, P. Yue, *Chem. Eng. Sci.* 59 (2004) 5269–5275.
- [33] J. Feng, X. Hu, P.L. Yue, *Environ. Sci. Technol.* 38 (2004) 269–275.
- [34] M. Bobu, I. Siminiceanu, E. Lundanes, *Anal. St. Univ. Al. I. Cuza Iasi, s. Chim., XIV* 1 (2006) 13–20.
- [35] J. Feng, X. Hu, P.L. Yue, *Water Res.* 40 (2006) 641–646.
- [36] S. Diplas, J. Lehmann, S. Jorgensen, T. Valand, J.F. Wants, J. Taflo, *Surf. Interface Anal.* 37 (2005) 459–465.
- [37] J.F. Moulder, W.F. Stickle, P.E. Sobol, *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corp., Physical Electronics Division, New York, 1992.
- [38] L.A. Cardoza, C.W. Knapp, C.K. Larive, J.B. Belden, M. Lydy, D.W. Graham, *Water Air Soil Pollut.* 161 (2005) 383–398.
- [39] J. Pignatello, *Environ. Sci. Technol.* 26 (1992) 944–951.
- [40] H. Gallard, J. De Laat, B. Legube, *New J. Chem.* 22 (1998) 263–268.
- [41] W.Z. Tang, C.P. Huang, *Environ. Technol.* 17 (1998) 1371–1378.
- [42] A. Safarzadeh-Amiri, J.R. Bolton, S.R. Cater, *J. Adv. Oxid. Technol.* 1 (1996) 18–26.
- [43] S.-F. Kang, C.-H. Liao, S.-T. Po, *Chemosphere* 41 (2000) 1287–1294.
- [44] M. Perez, F. Tonades, X. Domenech, J. Peral, *Water Res.* 36 (2002) 2703–2710.
- [45] P.R. Gogate, A.B. Pandit, *Adv. Environ. Res.* 8 (2003) 553–597.
- [46] I. Siminiceanu, M. Bobu, *Actes du Deuxieme Colloque Franco-Roumain de Chimie Appliquée CoFrRoCa*, Bacău, Romania, 2002.
- [47] J. Sunderland, C.M. Tobin, A.J. Hedges, A.P. MacGowan, L.Q. White, *J. Antimicrob. Chem.* 47 (2001) 271–275.